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(54) **New three-way catalysts with PT, RH and PD, each supported on a seperate support.**

(57) New catalysts for catalytic conversion of CO, light hydrocarbons and nitrogen oxides comprising a 1-layer/3-parts catalyst and/or a 3-layer catalyst, where Rh is supported on W⁶⁺-doped-TiO₂, Pd supported on Y₂O₃-doped-ZrO₂ and Pt supported on SiO₂ or γ-Al₂O₃ or Y₂O₃-doped-ZrO₂, were found to be significantly more active and durable than the

known commercial ones.

The new catalysts require smaller quantities of PGM in order to achieve the same activity as known ones and, in addition, present longer lifetime. They may be used for example for automobile emission control and/or for the treatment of industrial and power generation stations emissions.

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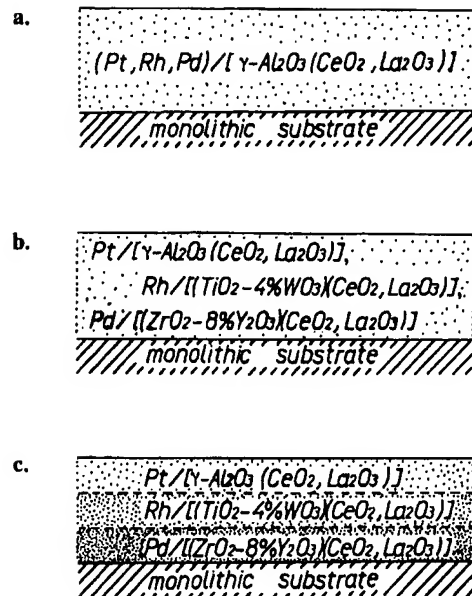


FIGURE 5

This invention refers to a new monolithic three-way catalytic converter with optimized distribution of precious metals within three separate washcoat layers and to its application to automotive exhaust treatment and to the treatment of industrial and power generation stations waste gases containing carbon monoxide, light hydrocarbons and nitrogen oxides. The new catalytic converter can be significantly more active and durable than the commercial ones and can thus require smaller quantities of noble metals. The activity of the catalyst is enhanced by application of two concepts, which recently have been developed in our laboratories: the phenomenon of Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA) and the phenomenon of Dopant-Induced Metal Support Interactions (DIMSI). Thus, optimal pairs of precious metal-support materials are specified, which provide maximum activity. These are: Pt/ γ - Al_2O_3 , Rh/ W^{6+} -doped TiO_2 and Pd/ $\text{ZrO}_2(\text{Y}_2\text{O}_3)$. In addition, these slurries of optimal pairs of metal and support are loaded separately in a monolithic support, forming three washcoat layers; the first layer containing Pd, the intermediate containing Rh, and the upper layer containing Pt. This configuration provides high durability due to higher resistance to poisoning, (protection of Rh and Pd in internal layers) and prevention of undesirable alloy formation. In this way the resulting catalyst exhibits higher activity and enhanced durability.

Background of the Invention

The use of automotive exhaust catalytic converters, during the last 20 years, in the control of atmospheric pollution from internal combustion engines has proved their serviceability and efficiency. However, the use of platinum group metals (PGM) as the active phase of the converters, makes their continuous improvement necessary, mainly for economic and environmental reasons. The main problem is related to the use of Rh, which is not only very expensive, but also very rare. The other PGM metals, Pt and Pd, are cheaper and they are available in greater amounts, but their continuously increased use makes them more expensive. On the other hand, catalytic converters suffer from poisoning and thermal ageing which makes their useful lifetime short and their replacement necessary. Consequently, catalysts which are active at low temperatures, and tolerant of high temperatures and poisons are needed, (e.g. K.C. Taylor, CHEM-THECH, 630 (1990); J.T. Kummer, J. Phys. Chem. 90, 4747 (1986).

The improvement of the activity of PGM catalysts depends mainly on their dispersion on support materials (washcoat), which are usually of high surface area, and on the possible presence of

special additives and stabilizers. Although the activity enhancement due to an increase in dispersion of PGM automotive exhaust catalysts is well known, the effect of the nature of the washcoat has not been sufficiently examined. In recent years, however, Verykios and his coworkers (1987, 1988, 1989, 1989 a,b) and Vayenas and his coworkers (1988, 1988 a,b, 1989, 1990) have shown that the activity of metal crystallites can be significantly enhanced if these are dispersed on doped semiconductive carriers or on solid electrolyte materials, respectively.

In the former case, semiconductive metaloxides, such as TiO_2 , are doped with cations of higher valence, such as W^{6+} , Ta^{5+} and Sb^{5+} , at low concentration levels. The doped materials are used as carriers in the formulation of metallic catalysts. As a result of an electronic interaction developing at the metal-semiconductor interface, which results in electron transfer from the support to the metal particles, the chemisorptive and catalytic properties of the metal surfaces are dramatically altered (Dopant-Induced Metal-Support Interactions or DIMSI phenomenon). Thus, the specific activity of Rh dispersed on higher valence doped TiO_2 , in CO hydrogenation is enhanced by a factor of 20, in CO oxidation by a factor of 10, etc. Similar behavior has been observed over Pd, Ru and Ir. It has also been observed that metal particles dispersed on higher valence doped TiO_2 carriers exhibit enhanced resistance to sulfur poisoning.

In addition to the DIMSI phenomenon described above, the phenomenon of Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA), developed by Vayenas and coworkers, is also applied towards the design of efficient automotive exhaust catalytic converters. The NEMCA phenomenon is based on the possibility of altering the work function of metallic or metal oxide catalysts by electro-chemical supply or withdrawal of ions to or from the surface by application of external potential in an electro-chemical cell of the type: reactants, electrode-catalyst/solid electrolyte/reference electrode. Such solid electrolytes are the yttria-stabilized zirconia ($\text{ZrO}_2/8 \text{ mol\% } \text{Y}_2\text{O}_3$ or YSZ), the $\text{ThO}_2/8 \text{ mol\% } \text{Y}_2\text{O}_3$, CeO_2 (La_2O_3), β'' - Al_2O_3 etc. It has been observed recently that metallic catalysts supported on materials of high ionic conductivity exhibit significantly enhanced activity which is comparable to that exhibited under the NEMCA phenomenon, although there is no external ion pumping. Thus, an "intrinsic" NEMCA effect can be developed, resulting in significant enhancement of catalytic activity. This latter concept is applied towards the design of exhaust catalysts.

Summary of the invention

In this invention a more active catalytic converter is described, as developed by application of the above concepts. The catalyst consists of Rh supported on W^{6+} -doped- TiO_2 , Pd supported on Y_2O_3 -doped- ZrO_2 and Pt supported on SiO_2 or $\gamma-Al_2O_3$ or Y_2O_3 -doped- ZrO_2 . These catalyst-support pairs were found to give maximum activity for the three-way reactions of the type:

- Oxidation of CO to CO_2
- Oxidation of light hydrocarbons (HC) to CO_2
- Reduction of NO_x to N_2

These reactions are of great importance not only in automotive exhaust gas treatment but also for the purification of the emissions containing CO, HZ and NO_x of many chemical industries and thermal power generating facilities.

The three metal-support pairs described above are formulated in a macroscopically uniform catalyst which can then be used either in the form of pellets or can be applied as a washcoat on the walls of the channels of a monolithic honeycomb type substrate. This configuration is hereafter denoted as "1-layer/3-parts" catalyst. The three metal-support pairs described above can also be formulated as three separate layers supported on monolithic honeycomb type substrates in the following sequence:

upper layer:

Pt/ $\gamma-Al_2O_3$ (CeO_2 , La_2O_3)

intermediate layer:

Rh/ W^{6+} -doped- TiO_2 (CeO_2 , La_2O_3)

lower layer:

Pd/ Y_2O_3 -doped- ZrO_2 (CeO_2 , La_2O_3)

where the lower layer is in contact with the monolithic substrate, which can be made from cordierite or other suitable, e.g. metallic, material and where CeO_2 and/or La_2O_3 are added as catalyst promoters which is well known to practitioners of this art. This novel configuration is hereafter denoted as "3-layer" catalyst.

The two catalysts described above, i.e. the "1-layer/3-parts" catalyst and the "3-layer" catalyst, are new and their main differences from all catalysts of similar type are described in detail below in the following illustrative, but not limiting "Detailed description of specific embodiments" section.

Brief description of the drawings

Figure 1: Maximum measured CO oxidation rate to CO_2 expressed as turnover frequency (s^{-1}), i.e., molecules CO reacting per surface metal atom per s, for fifteen catalysts consisting of all combinations of Rh, Pd and Pt supported on five chosen

supports.

Figure 2: Maximum measured C_2H_4 oxidation rate to CO_2 and H_2O expressed as turnover frequency (s^{-1}), i.e. molecules C_2H_4 reacting per surface metal atom per s for the fifteen catalysts of Figure 1.

Figure 3: Maximum measured NO reduction rate to N_2 by CO, expressed as turnover frequency (s^{-1}), i.e. molecules NO reacting per surface metal atom per s for the fifteen catalysts of Figure 1 and 2.

Figure 4: Effect of catalyst support on the light-off temperatures of CO oxidation, C_2H_4 oxidation, NO reduction and N_2 production at the stoichiometric point of operation.

Figure 5: Schematic representation of (a) a current state-of-the-art type catalyst with the usual $\gamma-Al_2O_3$ support (b) the new "1-layer/3-parts" catalyst where each of the three noble metals is supported on the appropriately chosen support and the three supports are mixed and (c) the new "3-layer" catalyst where each of the three metals is supported on the appropriately chosen support and the three supports are coated on the substrate in the sequence shown in the Figure.

Figure 6: Comparative results of the light-off temperatures of the three catalysts of Figure 5 at the stoichiometric point of operation.

Detailed description of specific embodiments

In this invention, a more active automobile catalytic converter is described, as developed by application of the metal-support interaction concepts described in the "background of the invention" section. First, the optimal pairs of each metal-support are specified in terms of CO oxidation, light hydrocarbons oxidation and NO_x reduction activity (see example 1). Five different supports were examined; two inert: TiO_2 (rutile) and SiO_2 , the usual commercial support: $\gamma-Al_2O_3$, and two modified: YSZ and TiO_2 doped with W^{6+} cations of variable concentration. Three PGM were examined; Pt, Rh and Pd. It was found in this work, that the nature of the support has a great effect on the activities of the metals. The following order of decreasing activity, for the above three reactions was observed:

Rh: W^{6+} -doped TiO_2 > YSZ > $\gamma-Al_2O_3$, SiO_2 > TiO_2

Pd: YSZ > $\gamma-Al_2O_3$ > W^{6+} -doped TiO_2 , SiO_2

> TiO₂

Pt: SiO₂ > γ -Al₂O₃, YSZ > TiO₂ > W⁶⁺-doped TiO₂

It is concluded that if a single support is selected for all metals, this must be the YSZ (NEMCA support). This formulation of an automotive exhaust catalytic converter gives better results as compared to a formulation in which a commercial support is used (see example 2a).

The results concerning the activity of metal-support pairs gave to us an idea to use separate supports for each PGM in order to maximize total activity. Thus, Rh is supported on W⁶⁺ doped TiO₂, Pd on YSZ and Pt on SiO₂, γ -Al₂O₃ or YSZ. This idea was applied to monolithic structures forming a catalyst containing three layers of washcoats, each washcoat containing a different PGM. A three-way catalytic converter formulated in this manner exhibits better activity than the commercial one, which has the same amount of PGM but supported on γ -Al₂O₃ (see example 2b). The proposed order of placing of the different layers is the following: first the layer containing Pd, dispersed on YSZ, the intermediate layer containing Rh, dispersed on W⁶⁺ doped TiO₂, and the upper layer containing Pt dispersed on γ -Al₂O₃. This order maximizes the resistance of the catalyst against poisons, because of protection of Rh and Pd, which are sensitive to poisons, and decreases the thermal ageing because of prevention of undesirable alloy formation between Pt and Pd.

This invention formulates a new catalyst which requires smaller quantities of PGM in order to achieve the same activity as the commercial catalyst and it presents, in addition, longer lifetime. The present invention relates to conversion of automotive emissions, and, more generally, to three-way reactions of the type:

- Oxidation of CO to CO₂
- Oxidation of light hydrocarbons (HC) to CO₂
- Reduction of NO_x to N₂,

which could also interest many industries which have problems of purification of emissions containing CO, HC and NO_x.

The present invention, e.g. the three-way catalyst which has this type of washcoat:

upper layer :

Pt/ γ -Al₂O₃ (CeO₂, La₂O₃)

intermediate layer:

Rh/W⁶⁺-doped TiO₂ (CeO₂, La₂O₃)

lower layer:

Pd/YSZ (CeO₂, La₂O₃)

supported on monolithic substrates from cordierite or other suitable, e.g. metallic, support, is a new catalyst and the main differences from all catalysts of similar type are the following:

1. The catalyst proposed from Hegedus and his coworkers (e.g. J.C. Summers and L.L.

Hegedus, J. Catal., 51, 185 (1978); L.L. Hegedus, and J.J. Gumbleton, CHEMTECH, 630 (1980)) consists of rings of Pt placed into the outer, Rh into the intermediate and Pd into the internal ring. The results showed sizable improvement in both steady-state and light-off temperature performance when the catalyst has an outer layer of Pt and an inner shell of Pd. These catalysts were pellet-type and the support was uniform γ -Al₂O₃. Thus the main differences with this invention are the non-uniform support (γ -Al₂O₃, W⁶⁺-doped TiO₂ and YSZ; each containing the more suitable PGM) and that these ideas are applied to monolithic types of support.

2. Serious differences also exist with the catalyst proposed by Nippon Molybdenum KK, Japanese Appl. 4/161,249, which uses unique support (active Al₂O₃) for all metals, supported on monolith. They place first Pd and possibly Ce oxide, they rest a layer without precious metals, and then they place on the upper layer Pt and/or Rh.

3. The catalyst proposed by Nissan Motor Co. LTD consists of a monolithic support coated either with a metal oxide containing Pt and/or Pd, itself coated with another metal oxide coating layer containing Rh (two layers-Japanese Appl. 4/161,248) or a first layer of Al₂O₃ containing Pt and/or Pd, a second layer of Al₂O₃ containing Rh supported or Zr oxide, and a third layer of Al₂O₃ containing Ir (uniform washcoat-Japanese Appl. 4/74,534).

4. Many other inventions (e.g. Nippon Shokubai Co. LTD, European Appl. 494,591 A; Agency of Ind. Sci. Tech., Japanese Appl. 4/78,442; Babcock-Hitachi K.K., Japanese Appl. 4/118,049; Osaka Gas Co. LTD, Japanese Appl. 4/ 161,230; Cateler Kogyo K.K., Japanese Appl. 4/87,627; Allied-Signal Inc., U.S. Patent 5,116,800; NGK Insulators LTD European Appl. 485,180 A; etc) present catalysts which contain TiO₂ and/or ZrO₂, but not in the form of the present invention (e.g. doped-TiO₂ or stabilized ZrO₂) neither using separate layers for PGM application. In these works, a better performance is presented against usual commercial catalysts containing PGM uniformly dispersed on γ -Al₂O₃. In the present invention, an optimum formulation of the new catalyst is presented, which exhibits superior performance as compared to similar types of catalysts.

The above differences make the present invention new and innovative. The technical improvements of the new catalytic converter for automobile emissions control, makes it more active than the existing ones by using optimal distribution of precious metals (Pt, Rh, Pd) within three separate washcoat layers consisting of different materials.

Thus, the new catalyst, in order to meet the EEC emission standards, requires smaller quantities of noble metals. Since the cost of the noble metals accounts for approximately 50% of the cost of the converter, significant savings can be realized.

The following working Examples represent a more detailed description of the invention.

Example 1

All possible combinations of metal and support were formulated into supported metal catalysts. The metals were Pt, Rh and Pd, and the supports were γ -Al₂O₃, SiO₂, TiO₂, TiO₂ doped with W⁶⁺ and YSZ. The deposition of the metal on the support was carried out by the method of wet impregnation which is well-known to practitioners of this art. The produced catalysts were dried, calcined and reduced under H₂ flow at 400°C for 2hrs. In all cases the metal loading was 0,5%. The activity of these catalysts was studied for the reactions: CO oxidation, C₂H₄ oxidation and NO reduction, which represent the reactions taking place within a catalytic converter, under identical conditions.

The investigation of the activity of each metal was carried out by means of kinetic studies in a CSTR-type reactor. The reactor is fed with mixtures of CO/O₂/He, C₂H₄/O₂/He or NO/CO/He. The mixture composition and the temperature are the main independent variables. Gas analyses are made by means of GC and IR instruments. Specific reaction rates are computed based on the analysis of the feed and product mixtures.

Results of this work are shown in Figs. 1, 2 and 3, which refer to CO oxidation, C₂H₄ oxidation and NO reduction, respectively. In these figures the maximum production rate of CO₂, obtained over different metals dispersed on different supports are given. The rate of production of CO₂ is reported in the form of turnover frequency to make more fundamental comparisons.

Figs. 1-3 show that the supports have a great influence on the activity of all metals. A common conclusion from these results is that the activity of PGM is enhanced if these are supported on YSZ. On the other hand, a strong effect of doping of TiO₂ with W⁶⁺ cations is presented on Rh for all three reactions. This effect is lower on Pd and negative on Pt.

Example 2

A three-way monolithic catalyst was prepared as follows: Cordierite monolith structure, containing 64 square channels per square centimetre (supplied by Corning Glass) were coated with different washcoats.

Washcoat slurries were prepared by mixing the support powder with water in a high-speed blender for a certain period of time. Solid concentration, temperature and pH play an important role in deposition procedure as is wellknown to practitioners of this art. Monolith specimens with a length of 5 mm and 16 mm diameter were provided with a washcoat by impregnation, followed by drying, calcination and reduction as described above. The PGM phase was applied by direct impregnation by filling the monolith channels once with the solution of PGM precursors or, alternatively, by simultaneous application together with the support.

The activity of the monolithic catalysts was measured in an appropriate apparatus. The monolithic piece is placed in the middle of a quartz tube which is placed in a furnace. The reactor was fed with gas mixtures which simulate the compositions of common car emissions and contain CO, C₂H₄, NO and O₂, diluted in He. The concentration of O₂ is lower, higher, or equal to the stoichiometric one, required for complete combustion of CO and C₂H₄. The catalyst contains all the necessary active phases in order to present a three-way operation. The gas analysis is made by means of gas chromatography.

The conversion of each pollutant is measured at different temperatures. In all cases of NO reduction the yield of N₂ is also measured. As a measure of characteristic activity, the light-off temperature, T₅₀, which is defined as the temperature of the inlet gas at which the conversion of the reactant is 50%, is defined.

a) At first, we examined the activity of monolithic catalysts consisting of a single support, with ~25% washcoat, which had 0,5% Pt and 0,1% Rh. In this manner tested the influence of the supports: YSZ, W⁶⁺-doped TiO₂ and the commercial one, γ -Al₂O₃ (8% CeO₂). The activity of these catalysts is shown in Fig. 4. The catalyst prepared with the commercial washcoat (γ -Al₂O₃) presents lower light-off temperature in CO oxidation, but higher in all other reactions, namely C₂H₄ oxidation, NO reduction and N₂ production. On the other hand, the catalyst which employs YSZ as the washcoat material shows lower light-off temperatures, i.e. higher activity for all reactions except CO oxidation. On the contrary, the W⁶⁺-doped TiO₂ support presents the worse behavior, with higher light-off temperatures in all reactions, apparently due to its negative effect in Pt activity which is contained at higher quantities than Rh. Subsequently, the YSZ support should be preferred as a single washcoat material, compared to the others examined here. It must also be emphasized that the dispersion of the metals on YSZ and W⁶⁺-doped TiO₂ is lower than that on γ -

Al₂O₃. The dispersion can be increased using other preparation procedures and this will result in even higher activity of the catalysts.

b) In order to examine the idea of using separate supports for each PGM, three different monolithic catalysts have been prepared and tested: The first configuration (Fig. 5a), which represents a current state-of-the-art type catalyst, was prepared with all PGM dispersed on γ -Al₂O₃ - (6% CeO₂, 2% La₂O₃). The second configuration (Fig. 5b), which represents the new "1-layer/3-parts" catalyst, was prepared containing the same quantity of PGM. In this catalyst, Pt was dispersed on γ -Al₂O₃, Rh on W⁶⁺-doped TiO₂ and Pd on YSZ. The three supports with the appropriate metals were well-mixed and then applied onto the monolithic substrate. Finally, a third configuration was prepared (Fig. 5c), which represents the new "3-layer" catalyst and contained the same quantity of PGM. This catalyst had three layers of different washcoats with the three PGM dispersed in the appropriate support. In the inner part we place YSZ which contains Pd, in the intermediate layer we placed W⁶⁺-doped TiO₂ which contained Rh, and in the outer layer the commercial support (γ -Al₂O₃, 6% CeO₂, 2% La₂O₃) which contained Pt. The application of the wash coats was done successively, following all the stages, i.e., impregnation, drying and calcination. All these catalysts contain ~34% total washcoat by weight of monolith and 0,145% Pt, 0,160% Pd, 0,039% Rh by weight of total washcoat.

The activity of these catalysts in terms of their light-off temperature, T₅₀, is presented in Fig. 6. It is clearly shown that the catalysts with modified supports are more active than this prepared with the commercial support, γ -Al₂O₃. The "1-layer/3-parts" catalyst exceeds in activity the "3-layer" one, at least in these particular conditions of experiment. However, if we take into account the increased resistance to poisoning of the three-layer catalyst, this must be the correct direction in the development of improved automotive catalysts. The issue of reduced dispersion of the metals dispersed on YSZ and W⁶⁺-doped TiO₂ must again be pointed out. By proper preparation of Pd/YSZ and Rh/W⁶⁺-doped TiO₂ washcoats, their activity can be improved significantly. Many techniques for improving the dispersion of supported metal catalysts are known.

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Allied-Signal. Inc., U.S. Patent No. 5,116,800.
NGK Insulators LTD, European Appl. No. 485,180 A.

Claims

1. Catalyst for the automotive exhaust treatment and the treatment of industrial and power generation stations waste gases by three-way reactions of the type of CO and light hydrocarbons oxidation and reduction of NO consisting of well-dispersed Rh, Pd and Pt each supported on a different catalyst support, characterized in that the three metal-support pairs are formulated in a macroscopically uniform catalyst which can then be used either in the form of pellets or can be applied as washcoat on the walls of the channels of a monolithic honeycomb type substrate (1-layer/3-parts

catalyst) or can be formulated as three separate layers supported on monolithic honeycomb type substrates in the following sequence:

upper layer:

Pt/ γ -Al₂O₃ (CeO₂, La₂O₃)

intermediate layer:

Rh/W⁶⁺-doped-TiO₂ (CeO₂, La₂O₃)

Lower layer:

Pd/Y₂O₃-doped-ZrO₂ (Ce₂O₃, La₂O₃)

where the lower layer is in contact with the monolithic substrate, which can be made from cordierite or other suitable, e.g. metallic, material and where CeO₂ and/or La₂O₃ are added as catalyst promoters (3-layer catalyst).

scribed in claims 1, 2, 3, 4, 5, 6 and 7 and its use.

2. A catalyst as in claim 1 where Rh is supported on W⁶⁺-doped-TiO₂, Pd is supported on Y₂O₃-doped-ZrO₂ and Pt is supported on γ -Al₂O₃.
20
3. A catalyst consisting of well-dispersed Rh, Pd and Pt, or Rh and Pt, or Pd and Pt all supported on Y₂O₃-doped-ZrO₂.
25
4. A catalyst as in claims 1, 2 and 3 where said catalysts are doped with CeO₂ or La₂O₃ or CeO₂ and La₂O₃.
30
5. A monolithic catalyst as in claims 1, 2, 3 and 4 where said catalyst is used as a washcoat deposited in the channels of a ceramic or metallic type support.
35
6. A monolithic catalyst as in claims 1, 2, 4 and 5 where the washcoat consists of three layers with each layer consisting of a support carrying a different metal.
40
7. A monolithic catalyst as in claim 6 where the washcoat consists of three layers: The first layer in contact with the ceramic or metallic honeycomb consists of Pd supported on Y₂O₃-doped-ZrO₂, the intermediate layer consists of Rh deposited on W⁶⁺-doped-TiO₂ and the top layer consists of Pt supported on γ -Al₂O₃.
45
8. A method for the preparation of the catalysts in claims 1, 5, 6 and 7 consisting of washcoat preparation, application and stabilization on monolithic honeycomb-type structures.
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9. An apparatus for automotive exhaust treatment comprising of catalysts described in claims 1, 2, 3, 4, 5, 6 and 7 placed in an appropriate metallic canister and its use.
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10. An apparatus for industrial and power plant emission treatment comprising of catalysts de-

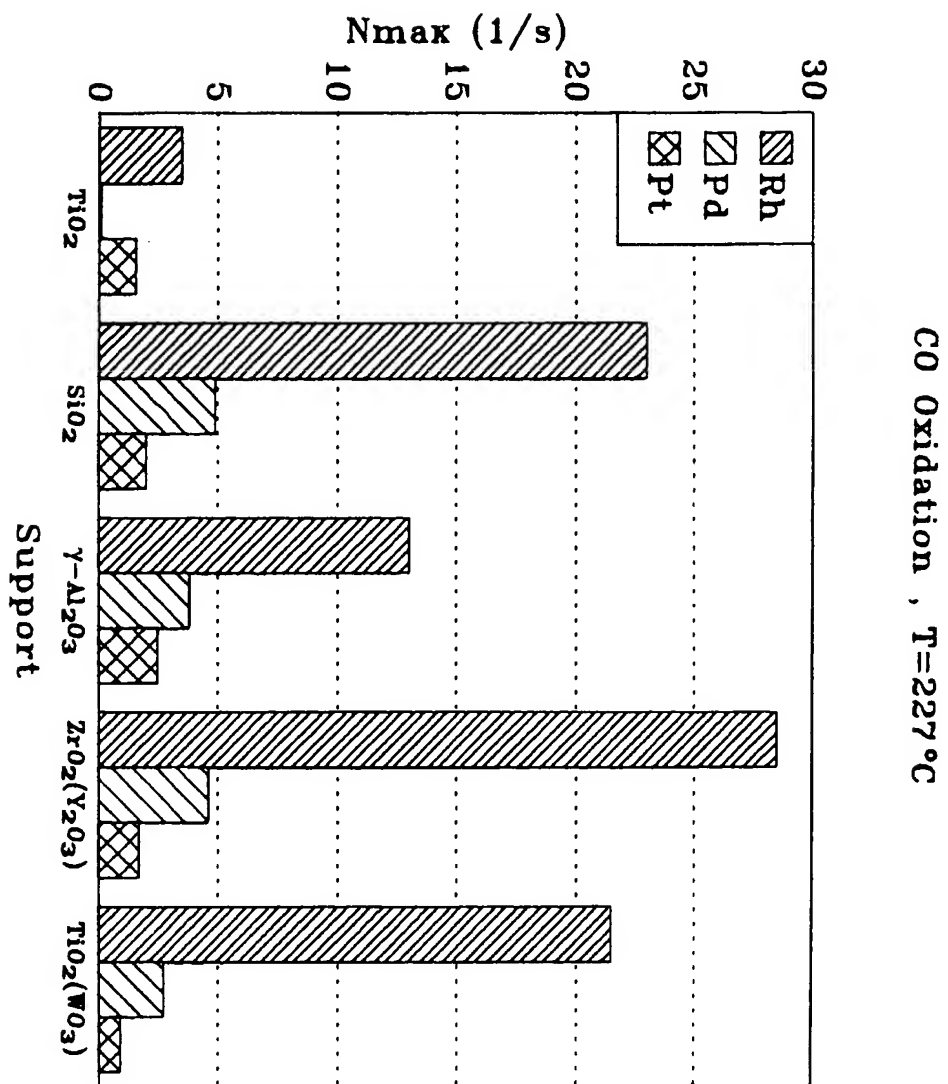


FIGURE 1

C_2H_4 Oxidation , $T=320^\circ C$

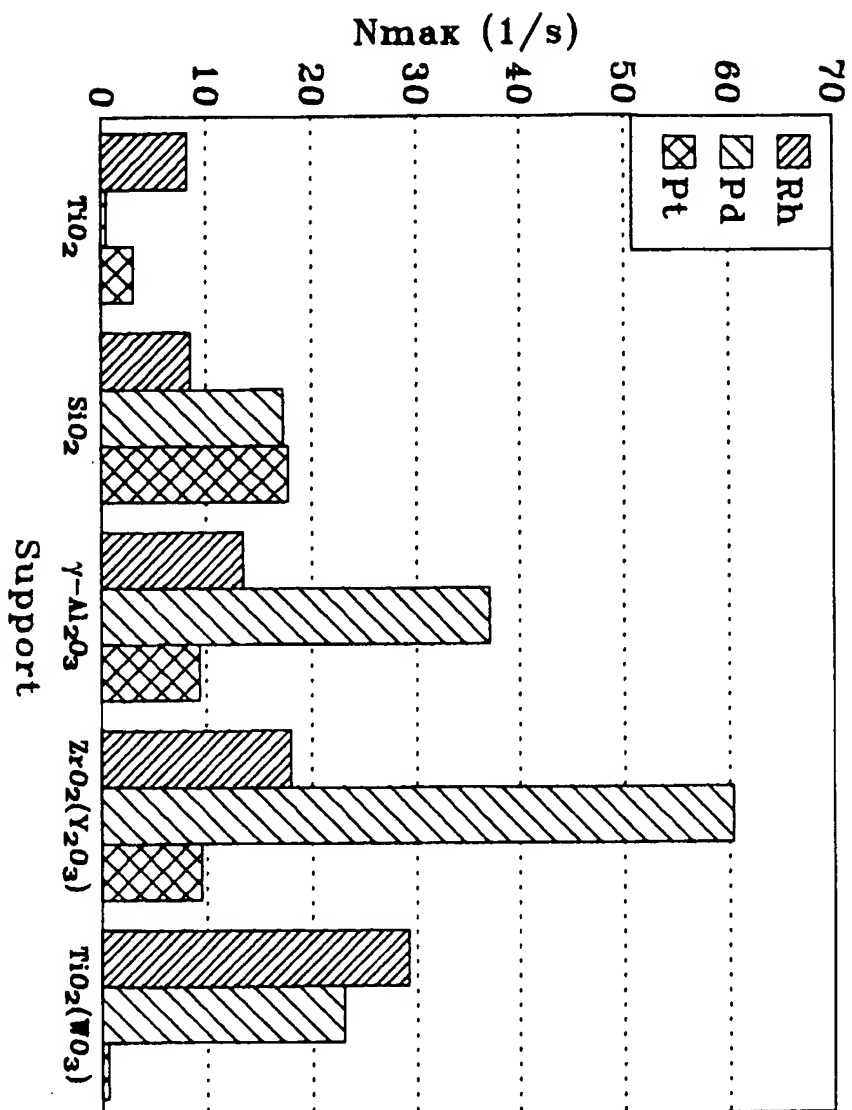
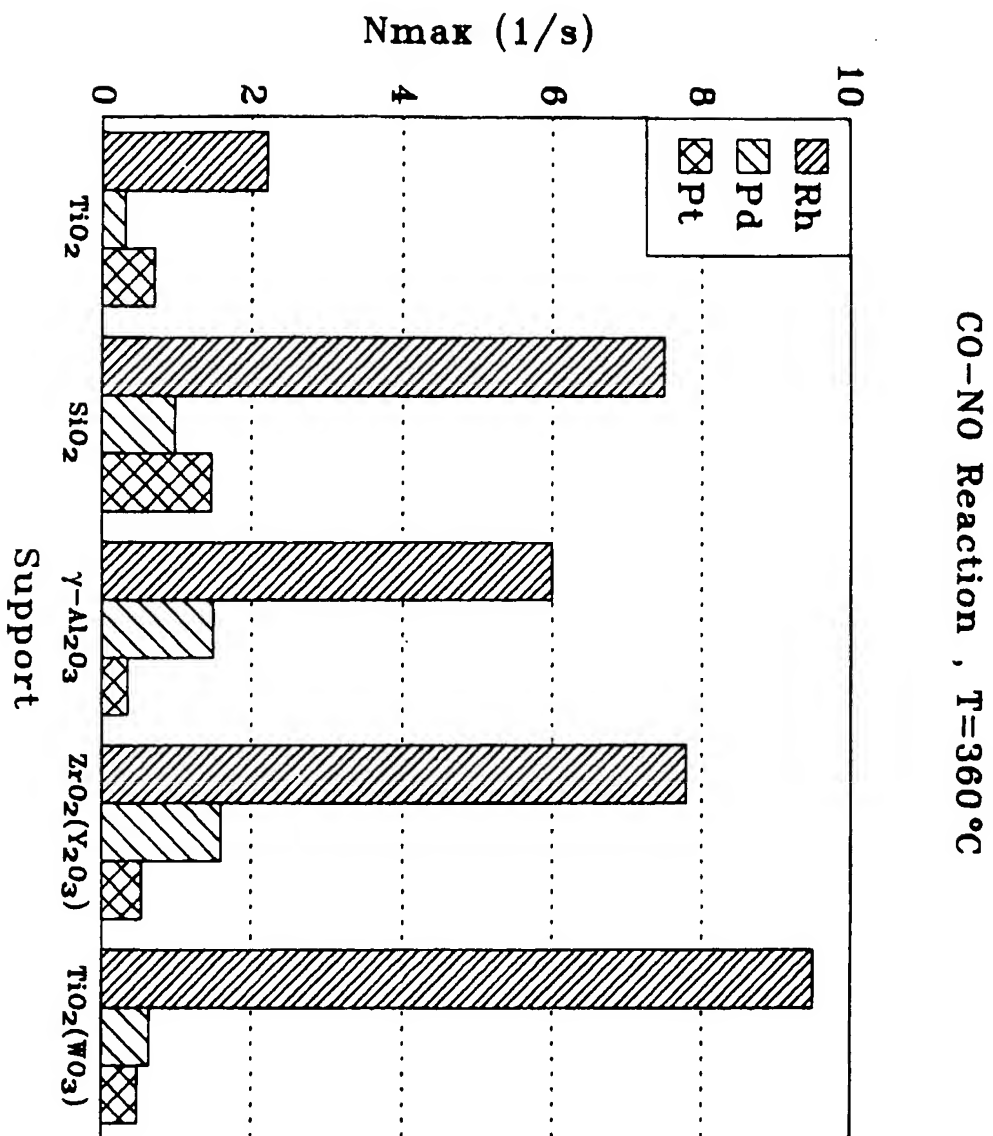


FIGURE 2

**FIGURE 3**

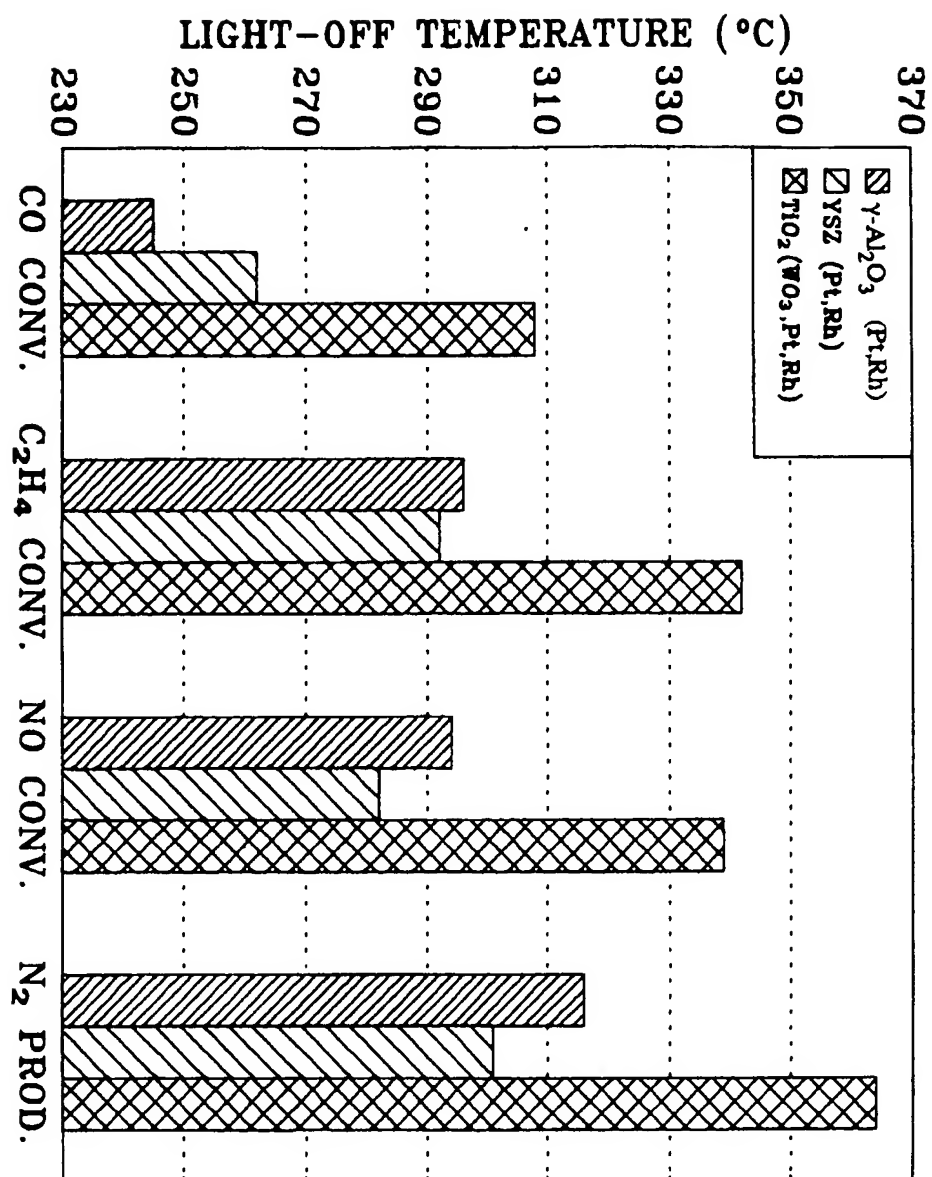
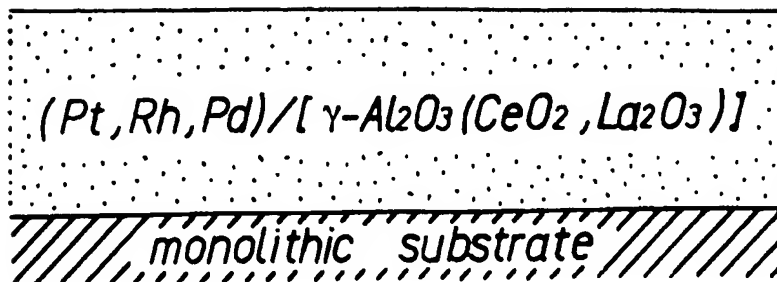
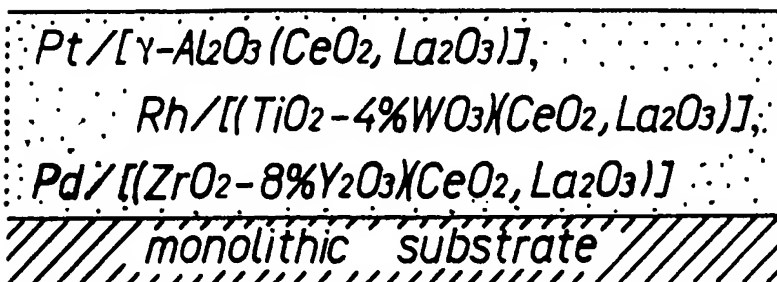


FIGURE 4

a.



b.



c.

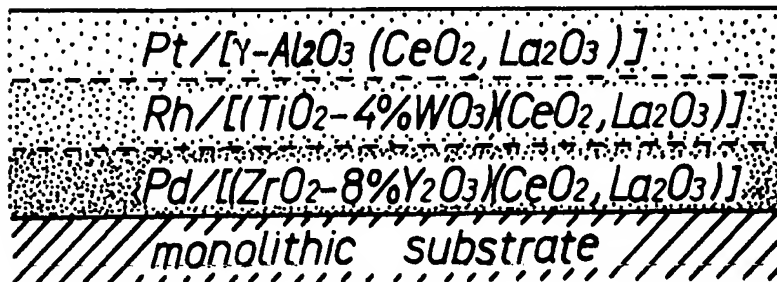


FIGURE 5

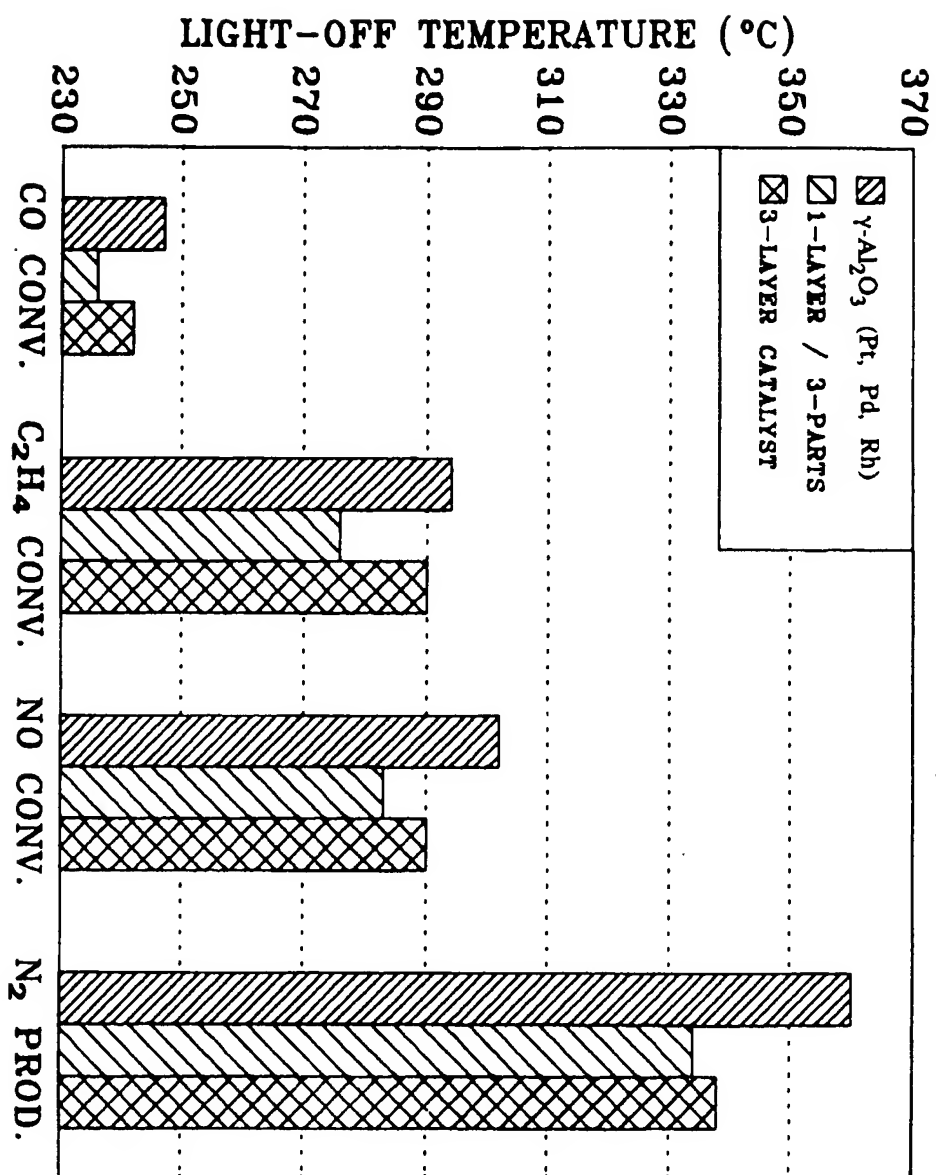


FIGURE 6



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 60 0002

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|---|---|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
| X | US-A-5 232 890 (PARTHA S. GANGULI) * claims * | 3, 4 | B01D53/94 B01J23/56 B01J37/02 |
| A | FR-A-2 595 265 (PRO-CATALYSE) * claims * | 1, 10 | |
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| A | EP-A-0 393 612 (ENGELHARD) | | |
| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.6) |
| | | | B01D B01J |
| The present search report has been drawn up for all claims | | | |
| Place of search THE HAGUE | | Date of completion of the search 16 June 1994 | Examiner Bogaerts, M |
| CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document | | | |